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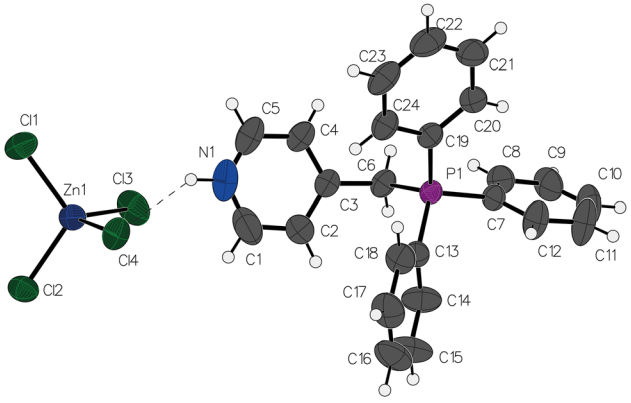
Crystal structure of 4-((triphenylphosphonio)methyl)pyridin-1-ium tetrachloridozincate(II), $C_{24}H_{22}Cl_4NPZn$



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Abstract

$C_{24}H_{22}Cl_4NPZn$, triclinic, $P\bar{1}$ (no. 2), a = 10.3047(9) Å, b = 10.7962(8) Å, c = 12.8277(11) Å, α = 71.763(3)°, β = 76.660(3)°, γ = 76.793(3)°, V = 1299.86(19) Å^3, Z = 2, $R_{gt}(F)$ = 0.0275, $wR_{ref}(F^2)$ = 0.0749, T = 293(2) K.

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The molecular structure is shown in the figure. Table 1 contains the crystallographic data and displacement parameters can be found in the cif-file attached to this article.

Table 1: Data collection and handling.

Crystal:	Clear light yellow block
Size:	0.18 × 0.16 × 0.16 mm
Wavelength:	Mo $K\alpha$ radiation (0.71073 Å)
μ:	1.43 mm^{-1}
Diffractometer, scan mode:	Rigaku, ω scans
θ_{max}, completeness:	28.3°, 100 %
$N(hkl)_{measured}$, $N(hkl)_{unique}$, R_{int}:	87793, 6473, 0.056
Criterion for I_{obs}, $N(hkl)_{gt}$:	$I_{obs} > 2\ \sigma(I_{obs})$, 5644
$N(param)_{refined}$:	284
Programs:	Rigaku[1], SHELX[2,3], Olex2[4]

1 Source of materials

A mixture of 4-((triphenylphosphonio)methyl)pyridin-1-ium chloride (0.01 mmol) and zinc chloride ($ZnCl_2$, 0.01 mmol) was dissolved in absolute ethanol (4 mL). Concentrated hydrochloric acid (HCl, ca. 0.5 mL, 36 % w/w) was then added to the solution. The resulting mixture was stirred at room temperature for approximately 30 min. The solvent (ethanol and excess HCl) was subsequently removed under a gentle stream of nitrogen gas or by controlled evaporation at ambient temperature. Crystals of the title compound formed upon complete evaporation of the solvent mixture.

2 Experimental details

The structure was solved by Direct Methods using SHELXT[2] and refined anisotropically for all non-hydrogen atoms using full-matrix least-squares methods (SHELXL[3]) within Olex2.[4]

3 Comment

Single-crystal X-ray diffraction (SCXRD) studies of triphenylphosphonium derivatives and their inorganic hybrid materials provide indispensable atomic-level insights crucial for advancing functional material design.[5–7] These analyses unambiguously elucidate the precise coordination geometry around metal centers (e.g., zinc in this case), the detailed conformation of the complex organic cation, and critical metrics like bond lengths, angles, and torsion angles.

As illustrated in the figure, the title compound features a phosphorus atom bearing four substituents: three phenyl rings and one 4-methylpyridin-1-ium group. The planes defined by

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these four groups are not coplanar. The dihedral angles formed between the plane of the 4-methylpyridin-1-ium ring and those of the three phenyl rings are 52.0°, 63.2°, and 30.5°, respectively. This staggered orientation contributes to a more compact molecular packing arrangement.[8,9]

Within the $[ZnCl_4]^{2-}$ unit, the Zn–Cl bond lengths range from 2.25 to 2.31 Å, indicative of a tetrahedral geometry.[10–12] Significantly, the inorganic anion and the organic 4-((triphenylphosphonio)methyl) pyridin-1-ium cation adopt an interleaved arrangement, forming a distinct organic-inorganic hybrid structure. This study provides valuable insights and foundational support for the design and development of novel organic-inorganic hybrid materials.

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